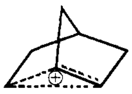
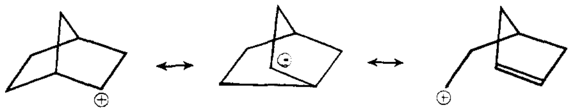
tive charge in the acylation reaction is divided between the positions *ortho* and *para* to the incoming group, and the geometry for hyperconjugation in the *para*-substituted norbornyl group is expected to be only "good." In contrast, in the solvolysis of *exo*-2-norbornyl derivatives the charge is highly localized and the developing p orbital from the *exo* leaving group is aligned parallel to the C_6–C_1 bond. This parallel configuration is optimum for stabilization through hyperconjugation.[4] Therefore, it would not be unexpected for the developing *exo*-2-norbornyl cation to receive several times the stabilization observed in the acylation reaction, *i.e.*, the norbornyl cation might receive 2–3 or more kcal/mole "extra" hyperconjugative stabilization because of the presence of more than the normal amount of p character in the C_1–C_6 bond.

Although the geomerty is optimum for hyperconjugative stabilization of the developing p orbital in the *exo*-2-norbornyl cation, the developing p orbital in the generation of the *endo*-2-norbornyl cation is in a geometrically less favorable position for C–C hyperconjugation with the C_1–C_7 bond, while overlap with the C_6–C_1 bond is virtually impossible.[5] Therefore, the *endo* compound is expected to react slower than the *exo* derivative. Similarly, the intermediate reactivity of 2-bicyclo[2.2.2]octyl derivatives is explained on the basis of normal hyperconjugative stabilization because of good geometry and small ring strain.

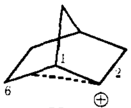
It is important to distinguish between C–C hyperconjugation and what is implied by participation in the nonclassical cationic sense. When the nonclassical intermediate IV is written, it represents a resonance hybrid of the canonical forms IVa → IVc.[6] Now valence bond theory depicts C–H hyperconjugation to an electron-deficient center as VI → VII.[4,7] By analogy, C–C hyperconjugation in the norbornyl cation would be depicted as IVa → IVc in valence bond terms. However, it is felt that these canonical forms involving σ-bond breaking are misleading when applied to hyperconjugation. Hyperconjugation should be considered as a phenomenon by which σ-bonding electrons are only partially delocalized to an electron-deficient center and these "participating" electrons formally remain in the σ bond. In other words, the movement of electrons and atoms is only slight but enough to provide stabilization at an adjacent developing electron-deficient center. Invoking the canonical forms (IVa → IVc) is not justified in the hyperconjugation model. In contrast to the nonclassical ion structure, the ion from the *exo* substrate has essentially retained its "classical" geometry. The partial σ-bond delocalization in the intermediate ion will be written as V, indicating at no time is the C_1–C_6 bond completely delocalized.



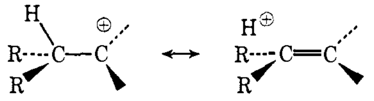
IV



IVa IVb IVc



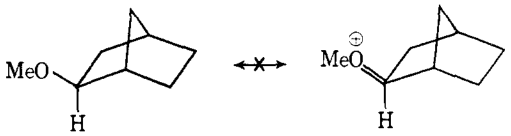
V



VI VII

Some examples of typical anomalies to the nonclassical ion picture can be seen in Table I.

The effect of a 1-anisyl or 6-methoxy substituent is incompatible with the nonclassical carbonium ion model. Both anisyl and methoxy are electron withdrawing inductively and will reduce the hyperconjunctive contribution of the C_1–C_6 bond,[8] and the decreased *exo* rate upon introduction of these substituents is predictable. It should be emphasized that the partial positive charge at position 1 or 6 in the hyperconjugation model cannot be delocalized by resonance of the type indicated in VIII. Since the hyperconjugation model assumes the bonding electrons are still formally localized on C_1 and C_6, stabilization by resonance as in VIII would effectively place ten electrons on C_6.



VIII

It is felt that the hyperconjugation model can explain much of the phenomena observed in the norbornyl system while also recognizing data anomalous to the nonclassical ion picture. Along with considerations of steric[3] and torsional[9] factors, the hyperconjugation model should be a highly predictive tool involving substituent effects.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP 6350X.

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[4] For example, M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[5] Electron delocalization is into the portion of the developing p orbital opposite the leaving group.

[6] G. D. Sargent, *Quart. Rev.* (London), 20, 301 (1966), and references therein.

[7] J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952.

[8] For the effect of substituents on hyperconjugative capacity, see, for example, J. R. Knowles and R. O. C. Norman, *J. Chem. Soc.*, 2938 (1961).

[9] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).

[10] National Institutes of Health Predoctoral Fellow, 1968–1969.

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An Electron Paramagnetic Resonance Spectral Study of Intramolecular Reactions of Aryl Radicals

Sir:

Recently developed methods[1,2] for the generation of free alkyl and aryl radicals within the cavity of an epr

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[1] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc., B*, 403 (1969).

[2] A. L. J. Beckwith and R. O. C. Norman, *ibid.*, 400 (1969).

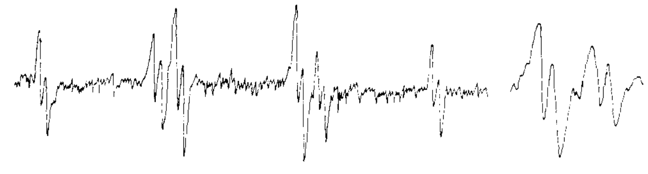


Figure 1. Epr spectrum of V, showing details of one multiplet recorded under slow scan.

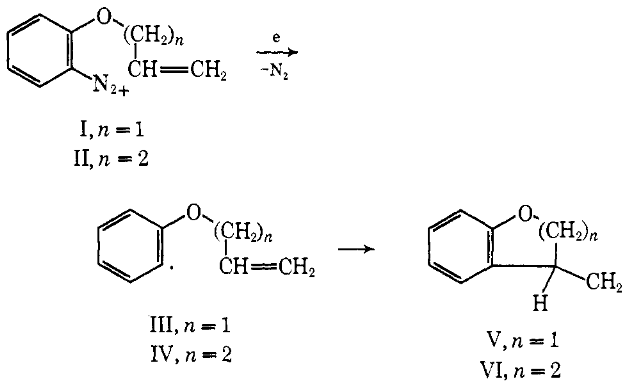
spectrometer using the flow technique provide a powerful tool for probing the mechanisms of radical reactions in solution. We now describe the first use of these methods to detect intramolecular radical reactions and the discovery thereby of two new transformations of suitably constituted aryl radicals.

When *o*-allyloxybenzenediazonium ion (I) in aqueous solution was reduced with Ti^{III} or $CO_2\cdot^-$ at pH ~8 as previously described[1] the recorded spectrum[3] (see Figure 1) had characteristics (see Table I) which defined the structure of the intermediate radical as V. The *g* value and α coupling constant are similar to those of free ethyl, but the β coupling constant is relatively low, thus indicating some restriction of free rotation about the C_α–C_β bond. The precise origin of the small γ coupling is not yet clear; further experiments are required to clarify long-range interactions in this type of radical. The same spectrum, but with much weaker signal strength, was recorded when I was reduced with $\cdot C(CH_3)_2OH$ derived from 2-propanol at low pH.[4]

Table I. Epr Spectral Data

Radical	Coupling constants, G $a_{\mathrm{H}\alpha}$	Coupling constants, G $a_{\mathrm{H}\beta}$	Coupling constants, G $a_{\mathrm{H}\gamma}$	*g* value
V	22.2	19.0	1.0	2.0025
VI	21.8	26.2		2.0025
IX	22.1	27.2		2.0025
X	~22.4	~27		ND[a]
XI	20.4	9.4		ND
XII	20.2	10.45		ND
XIII	20.2	22.6		2.0031

[a] Not determined.



Reduction of the homologous diazonium ion (II) with Ti^{III} at pH ~8 occurred rapidly and afforded the radical VI characterized by its epr spectrum (see Table I) which comprised a clear doublet of triplets. Addition to the reactant solutions of ethanol or of maleic acid, both of which react with aryl radicals,[1] neither changed the epr spectrum nor diminished its intensity.

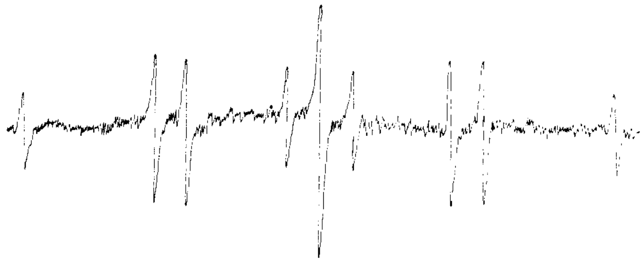


Figure 2. Epr spectrum of 2-phenoxyethyl radical (VII).

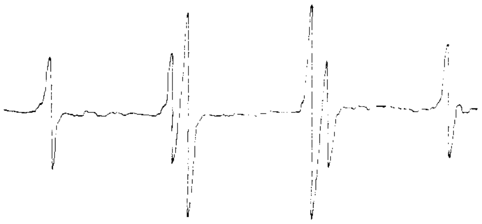


Figure 3. Epr spectrum of XIII.

The formation of V and VI is ascribed to cyclization of the appropriate aryl radicals (III, IV) generated in the usual way by one-electron reduction of the diazonium salts.[1] This intramolecular analog of the Meerwein reaction clearly proceeds with great rapidity since it competes effectively with hydrogen-atom transfer from ethanol or radical addition to maleic acid. The formation of V and VI from III and IV, respectively, evidently proceeds in a highly specific fashion for the recorded spectra showed no indication of signals which could be ascribed to radicals produced by cyclization of the aryl centers onto the remote termini of the olefinic bonds. It appears that in all these systems, like some of those involving alkenyl radicals,[5,6] the stereoelectronic requirements of the transition state take precedence over the thermochemical stability of the products as the factor controlling the direction of intramolecular radical addition.[5]

The spectrum of VI contained no signal attributable to the allylic radical which could conceivably be generated from IV by intramolecular 1,5-hydrogen atom transfer. Clearly, when both atom transfer and radical addition reactions are possible the latter is favored, but experiments with radicals containing suitable saturated side chains revealed that the former process may also occur and can be detected by epr spectroscopy.

Reduction of *o*-ethoxybenzenediazonium ion (VII) with Ti^{III} or $CO_2\cdot^-$ in the spectrometer gave a spectrum (see Figure 2) which established the presence of 2-phenoxyethyl radical (IX). Similar treatment of *o*-propylbenzenediazonium ion gave a very weak spectrum. The coupling constants could not be accurately determined, but their approximate values are compatible with the structure (X) assigned to the radical. In both of these systems the signal was destroyed by addition of ethanol to the reactant solutions, while addition of maleic acid gave new spectra consisting of strong doublets of doublets assigned to the appropriate maleate adducts (XI, XII).[1] Reduction of the diazonium ion

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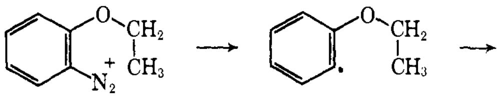
(3) Spectra were recorded on a Varian epr spectrometer using *p*-benzosemiquinone and Fremy's salt as standards for the determination of *g* values and splitting constants.

(4) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

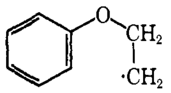
(5) D. L. Struble, A. L. J. Beckwith, and G. E. Gream, *Tetrahedron Lett.*, 3701 (1968).

(6) N. O. Brace, *J. Org. Chem.*, 32, 2711 (1967), and references cited therein.

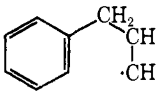
derived from 4-(*o*-aminophenyl)butyric acid gave an intense epr spectrum (see Figure 3) assigned to the radical XIII. The signal was unaffected by addition of ethanol or maleic acid to the reactant solutions.



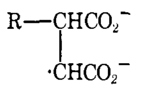
VII VIII



IX



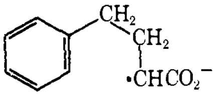
X



$R—\underset{\cdot CHCO_2^-}{CHCO_2^-}$

XI, R = *o*-EtOC$_6$H$_4$

XII, R = *o*-CH$_3$CH$_2$CH$_2$C$_6$H$_4$



XIII

The radicals IX, X, and XIII are clearly formed by 1,5-hydrogen atom transfer processes (*e.g.*, VIII → IX) proceeding through a six-membered cyclic transition state. In the absence of suitable activating substituents the reaction is relatively slow compared with possible intermolecular processes of aryl radicals, such as hydrogen atom abstraction from ethanol or addition to maleic acid, but it becomes the preferred reaction when the product radical is stabilized by an adjacent carboxylate group.

The foregoing experiments, the conclusions from which have been separately confirmed by analysis of products,[7] clearly establish the utility of epr spectrometry as a technique for investigating the mechanisms of radical reactions in solution.[7a]

Acknowledgment. This work was supported in part by the Australian Research Grants Committee. A. L. J. B. offers thanks for generous hospitality to the Chemistry Department, University of York, where some of the experimental work was conducted.

(7) A. L. J. Beckwith and W. B. Gara, *J. Amer. Chem. Soc.*, **91**, 5691 (1969).

(7a) NOTE ADDED IN PROOF. The use of epr spectrometry to study the cyclization of 5-hexenyl radical has been recently reported by J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969).

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Intramolecular Addition and Hydrogen Atom Transfer Reactions of Aryl Radicals

Sir:

In the preceding communication[1] we described the use of epr spectral techniques to detect the occurrence of intramolecular addition and hydrogen atom transfer reactions in suitably constituted aryl radicals. Further evidence in support of our conclusions is disclosed herein.

When *o*-allyloxybenzenediazonium borofluoride was reduced with Ti^{III} at pH $\sim$8 in a flow system,[2] or with radicals derived from methoxide or isopropoxide ion,[3] the products, identified and estimated by glpc,[4] were allyl phenyl ether (VI), 2,3-dihydro-3-methylbenzo[*b*]furan (IX), and polymeric materials. The yields of VI and IX formed by these methods were small (see Table I), but when *o*-allyloxyiodobenzene (II) was reduced with tributylstannane in benzene[5] a clean reaction occurred and, in most cases, IX was obtained in quantitative yield. Reduction of *o*-(3-butenyl)iodobenzene (III) with tributylstannane was similarly efficient (see Table II) and gave good yields of VII and X. In no case could we detect formation of six-membered cyclic products.

Table I. Reduction of *o*-Allyloxybenzenediazonium Ion and of *o*-Allyloxyiodobenzene

Expt	Compd[a]	Reducing agent	Yield, % IX	VI
1	I	$TiCl_3$[b]	11	2
2	I	MeO^-–MeOH[c]	30	<5
3	I	*i*-PrO^-–*i*-PrOH[c]	1.5	7
4	II	*n*-Bu_3SnH[d]	99	Nil
5	II	*n*-Bu_3SnH[e]	99	Trace

[a] Compound I as the borofluoride. [b] 0.008 *M* in water at pH $\sim$8.[1] [c] 2 *M*. [d] 0.172 *M*, in excess. [e] 0.69 *M*, in excess.

Table II. Reduction of *o*-3-Butenyliodobenzene with Tributylstannane[a] in Benzene at 135°

[III], *M*	[R_3SnH], *M*	Yield,[b] % VII	X
0.078	0.0	0	0
0.072	0.068	6	56
0.073	0.137	17	80
0.073	0.288	38	62
0.073	0.568	50	50

[a] Initiated with ADIB. [b] Mean results from duplicate experiments.

These results clearly indicate that aryl radicals containing a correctly disposed olefinic function readily cyclize by intramolecular addition. As expected on the basis of epr measurements such cyclization processes evidently proceed very rapidly. Thus, in expt 1, 2, 4, and 5 (see Table I) the high ratio of yields, % IX/% VI, suggests that cyclization of IV is much faster than its reduction by Ti^{III} or its abstraction of hydrogen from methanol or tributylstannane. Only 2-propanol appears to be sufficiently active as a hydrogen atom donor to intercept IV efficiently before it undergoes intramolecular addition.

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(1) A. L. J. Beckwith and W. B. Gara, *J. Amer. Chem. Soc.*, **91**, 5689 (1969).

(2) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc., B*, 403 (1969).

(3) J. F. Bunnett and H. Takayama, *J. Amer. Chem. Soc.*, **90**, 5173 (1968); *J. Org. Chem.*, **33**, 1924 (1968).

(4) Internal standards were used. Calibration curves were prepared using authentic compounds synthesized by unambiguous routes.

(5) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964), and references cited therein.